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porous bodies, phase conversion (often with consolidation), and plastic deformation. Formation and consolidation of diamond and cubic BN are only briefly noted since they are extensively addressed elsewhere. It is shown that powder outgassing can be an important problem for some of these processes. Particular attention is given to impact or shock treatment, especially compaction of powders, and to hot extrusion of ceramics, including conventional as well as hydrostatic extrusion. Next, possible future application of high pressure to processing of ceramics is addressed. Explosive compaction of ceramics, especially of certain tougher ceramic composites wherein a synergism may be effective is suggested. Then the past and potential application of high pressure in mechanically working and shaping ceramics is discussed, again in part focused on processing tougher ceramic composites.

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A

APPLICATION OF HIGH PRESSURES TO CERAMICS

ABSTRACT

The use of pressure, an important variable in the study and especially the processing of ceramics, is first briefly reviewed showing that most pressures used are well below the high pressure range. Three areas of high pressure studies of ceramics that can be important in understanding ceramic behavior and can also be useful in specialized ceramic processing are then briefly outlined: compaction of powder or porous bodies, phase conversion (often with consolidation), and plastic deformation. Formation and consolidation of diamond and cubic BN are only briefly noted since they are extensively addressed elsewhere. It is shown that powder outgassing can be an important problem for some of these processes. Particular attention is given to impact or shock treatment, especially compaction of powders, and to hot extrusion of ceramics, including conventional as well as hydrostatic extrusion. Next, possible future application of high pressure to processing of ceramics is addressed. Explosive compaction of ceramics, especially of certain tougher ceramic composites wherein a synergism may be effective is suggested. Then the past and potential application of high pressure in mechanically working and shaping ceramics is discussed, again in part focused on processing tougher ceramic composites.

HIGH PRESSURES are applied to ceramics for a variety of reasons, which include phase transformation, deformation, or consolidation. Much of this is done for scientific purposes, but there is some existing, practical utilization, and potential for more, primarily in processing ceramics. The results of high pressure studies of ceramics and related materials, e.g. minerals, are extensively discussed and reviewed in the literature. Much less discussion and review of high pressure for processing of ceramics has been presented, except for processing of C and BN. The purpose of this paper is, thus, to discuss the application of high pressures to ceramic processing. In order to properly set the stage for this, it will be useful to briefly review the use of pressure in ceramic processing, as well as some aspects of high pressure studies of ceramics. However, before doing this, I will first define ceramics and discuss some of the potential growth in their application that can be an important motivation to use high pressures.

The term, Ceramic, as used in this paper means any inorganic, non-metallic solid, as broadly accepted by ceramists, government agencies, and many others in the materials field. I find it useful to note this definition since I have found some other scientists often have a much more proscribed, but less clear idea of what ceramics are. Thus,

ceramics are one leg of a triad of base materials that can be used by themselves or as constituents of composites. An important ramification of this definition, and hence of the scope of this talk, is that single crystals, as well as polycrystals, and glasses, or mixtures of these, that meet this definition will all be ceramics. Thus, both single - and poly - crystals of materials such as Al_2O_3 , SiC, TiB₂, BN, C, (diamond and graphite), etc., are ceramics. The latter two materials, BN and C, are of course two of the most important materials to which high pressures are applied for processing.

The many unique properties of ceramics such as the wide ranges of thermal and electrical conductivities (e.g. superconducting to outstanding dielectrics), hardness, and melting temperatures are important driving forces for significant application of ceramics. The impact that successful use of ceramics can have has greatly increased as shown by potential use in the energy field. This includes key materials for coal gasification and liquification, transport membranes such as ZrO_2 in fuel cells and oxygen sensors, and $\beta^2-Al_2O_3$ for high energy batteries. However, of even greater impact are the energy savings that successful use of ceramics in heat exchangers and heat engines can have. For example, high temperature components such as turbine vanes and blades, and diesel engine piston caps and cylinder liners are the key to efficiency improvements of 30-50%, often with other important potential benefits such as greater reliability, life, and large savings of scarce elements, and possibly of cost. The pacing issue in these as well as most other high technology ceramic applications is mechanical reliability, which depends critically on processing. As will be shown later, there may be important opportunities for high pressure processing to significantly improve mechanical reliability, especially as a result of recent concepts and developments.

OUTLINE OF THE DEMONSTRATED USE OF PRESSURE WITH CERAMICS

CONVENTIONAL PRESSURES FOR PROCESSING - Pressure is a basic variable in both the processing of ceramics and the understanding of their behavior. Consider first, conventional processing (primarily Section A of Table 1), which is only briefly outlined since this is extensively treated elsewhere, e.g. refs. (1-4)*. Ceramics are predominately made by consolidation of powders, most commonly by mechanical pressure. The most extensively used process is to consolidate powders at room temperature with pressure (called cold pres-

*Numbers in parentheses designate References at end of paper.

sing). The pressed powder part (called a green body) is then heated for sintering, i.e. bonding and further consolidation driven by reduction of solid surface area, e.g. by surface and bulk diffusion. Most cold pressing is done by uniaxial pressures in steel dies, but isostatic pressing using fluid pressure on powder in a rubber or plastic container is an important and growing method. A more limited, but growing approach to processing by powder consolidation is to combine pressing and heating. Combined uniaxial pressing and heating called hot pressing, and similarly use of gas pressure on a powder in suitable metal or glass envelopes or on sintered parts with only closed porosity called hot isostatic pressing (or HIPing) are also reviewed elsewhere (5-8). As noted in Table 1, fluid pressures may also be used in crystal growth, sintering, or annealing processes. However, these are more specialized, and are not addressed further here.

Table 1 - Typical Applications of Pressure in Processing of Ceramics

PROCESS	Common Pressure Ranges	
	(1000 psi)	(kb)
A) Consolidation of Powders		
1) Extrusion	5-10	0.3-0.7
2) Die Pressing	10-20	0.6-1.3
3) Isostatic Pressing	20-50	1.3-3.4
B) Overpressures for Sintering, Annealing, and Crystal Growth	0.1-5*	0-10-2*
C) High Temperature Densification		
1) Hot Pressing	3-6	0.2-0.4
2) Hot Isostatic Pressing	10-50	0.6-3.4
D) Hot Working		
1) Press Forging	3-12	0.2-0.8
2) Hot Extrusion	100-240	7-16

*Does not include special processing such as hydrothermal growth; an important, but specialized, process not treated in this paper.

The established uses of the above processes attest to their differing degrees of practicality that can yield a variety of very useful ceramics. However, there is substantial room for improvement, especially for demanding high technology applications. Use of higher pressures can in principle be one of the greatest improvements. These can give higher green densities which in turn can give higher final densities, or a lowering of sintering temperatures. Higher densities can improve mechanical properties, as can lowering temperatures if grain (crystallite) sizes are adequately reduced. High pressures and resultant densities may be particularly critical to sintering ceramic-ceramic composites that will be discussed later. However, die wall friction, and inhomogeneities can lead to many self limiting problems in cold pressing. Costs can be a critical issue in hot pressing or HIPing and, as will be illustrated later, adequate outgassing of powders can also become an important limitation.

The above processes do not result from any significant plastic flow. Application of processing methods that depend on extensive plastic flow within ceramics (as opposed to flow by relative motion of particles) have been quite limited, but show promise for further growth. These processes, which are reviewed in more detail elsewhere (8-10), are primarily compressive deformation, usually at modest rates (e.g. strain rates of 2×10^{-2}

min^{-1}), called press forging, and hot extrusion, often at rates similar to those for metals. While consolidation of powders by pressure used for deformation is possible and has some promise, the focus has been on deformation of bodies that were already solid to begin with. In fact, a substantial amount of interest has been on starting with single crystals to recrystallize them into polycrystalline bodies. This is done to have the advantage of the purity and absence of porosity in the crystal carried over to a polycrystalline body with its advantages, such as improved mechanical strength due to grain size effects. Extrusion has been feasible at conventional pressures only for soft, lower melting materials such as the alkali halides. On the other hand, press forging has been accomplished on a number of materials, including some very refractory ceramics, such as MgO , ZrO_2 , MgAl_2O_4 , and TiC , using quite high temperatures with conventional pres-

ures* of a few thousand psi (8-10), including simple shaping (11).

HIGH PRESSURE CONVERSION OR CONSOLIDATION OF CERAMIC POWDERS - The most extensive application of high pressures to ceramics is of course the making of diamond and cubic BN powder materials by pressure conversion from their hexagonal form. Also of growing application is the consolidation of polycrystalline compacts of these materials. While these are extremely important and interesting applications, they will not be reviewed here because of extensive attention to these topics elsewhere in this volume and in many other publications.

A few fine (e.g. 30-50 nm dia) ceramic powders have been consolidated to near theoretical densities at high pressures (8,12).

*Press forging is feasible at much lower pressures than extrusion since there is normally no lateral constraint on the bodies' flow in contrast to the high lateral constraint of extrusion. Further, the lower pressures of press forging can often be met by ceramic, especially graphite tooling, allowing use of hot tooling, and hence slow deformation rates and, thus keeping pressures low. This is in contrast to the high strength tooling for extrusion and related high deformation rates and hence higher pressures needed to keep that strength.

These include Al_2O_3 with 100-400 kb at 22°C and MgO with 70 kb at 22°C (8,12) or with 17 kb at 800-1000°C (8,13) (in contrast to temperatures of 1300-1500°C needed in conventional hot pressing). However, besides being confined to quite small samples, the resultant properties were quite poor. This is attributed to hydroxide, carbonate, and related impurities trapped in the bodies (8,14) resulting from the: 1) high active surface area of the fine powders that are more amenable to obtaining high densities; 2) lower temperatures of consolidation providing less driving force to remove the gases; and 3) possible pressure stabilization of the hydroxides, etc. Such problems illustrate a potential paradox of high pressure powder consolidation, namely that the use of fine powders for easier consolidation appears to be self-limiting due to greater surface contamination of such powders. Obviously, the nature and severity of this problem varies with the chemistry of the powder, but this is a serious problem for many important materials.

Limited studies of consolidation of SiC and Si_3N_4 powders have been carried out at high pressures (15-17). These materials do not sinter under normal conditions without the presence of sufficient quantities of additives or impurities, usually oxides. However, they will densify under high pressure at high temperatures, though much of this is by crushing. Thus, for example, Nadeau (15) reported reaching > 90% of theoretical density with 30 kb pressure at 22°C and 98% at 1500°C, but that interparticle bonding did not occur below 1500°C. The very restricted specimen size and very high cost put such pressing out of the realm of practical process, but it has been very useful to give greater insight into the sintering of these materials.

Consolidation of ceramic powders by high rate impact or shock methods has been of interest to overcome some of the limitations of static high pressure consolidation of ceramic powders and possibly open new opportunities of processing. About 20 years ago, there was considerable activity in applying these techniques to ceramics resulting in at least 20 different ceramic materials being investigated, but usually on a cursory level (5-7,18,19). While a fair amount of earlier work was done on explosive compaction, much of the work was done using a pneumatic driven impacting device called a Dynapak. There was some efforts to use the Dynapak device to forge bulk pieces of glass heated to about 600°C and impacted in dies preheated to 200-250°C, but these initial efforts were dropped due to shattering of the glass (18). Most work was, instead, on consolidation of powders contained in metal cans. Significant improvement in densities over those achieved by normal cold pressing were obtained by "Dynapaking" at room temperature, but serious cracking and even extensive shattering were

pervasive problems. Therefore, much of the work was focused on compaction at elevated temperatures in order to possibly eliminate the cracking or shattering and also in many cases to further improve consolidation and/or bonding between the particulates. While substantial progress was made in reducing cracking, it was generally not eliminated (5-7,18,19), Fig. 1. For example, even impacting LiF pellets in stainless steel cans after heating and outgassing at 650-750°C did not totally eliminate cracks though the resultant compacts were reported as being promising (18).

One of the most extensive investigations of "Dynapaking" of ceramic powders was for the development of dense agglomerates of UO_2 by itself or with other oxides for nuclear fuel purposes (20-25). Thus, sufficient material was compacted for fuel core loadings of at least two reactors. The loading for one of the (test) reactors used fused UO_2 grain that was ground to approximately -100 mesh and then mixed with limited quantities of fine UO_2 powder that had been oxidized to U_3O_8 in order to give a material with a net oxygen excess since this was found to give better plasticity at elevated temperatures. The material was then "Dynapaked" in 310 stainless steel cans. (These cans were used since they gave less oxygen loss of the UO_2 powder than other steel such as 304 at the outgassing conditions used, typically 1100°C for approximately one hour, prior to "Dynapaking".) The resultant "Dynapaked" UO_2 , although extensively cracked, was 97-99% dense in between the cracks (Fig. 1). In this

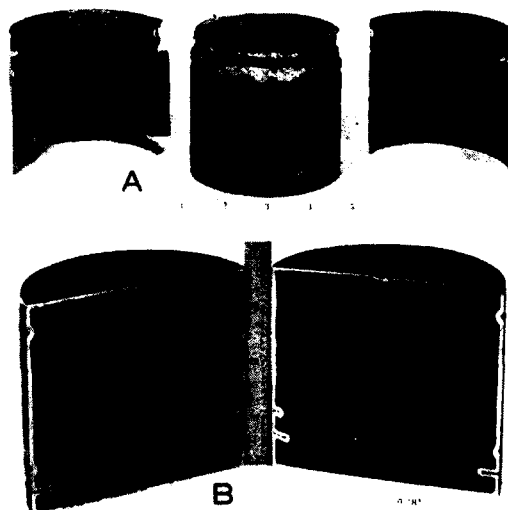


Fig. 1 - Dynapaked UO_2 fuel. A) Dynapaked billet of over 7 kg with the metal can removed. B) A sectioned billet revealing the extensive cracking that typically occurred in this operation. Note that the cracks do not show up on the surface of billet A) but would be found inside as in B). Billets compacted at 1100°C. Photos courtesy of D.W.Brite, Battelle Pacific Northwest Lab.

* This device, developed by General Dynamics Corp., uses an expanding gas to drive a piston and ram assembly to velocities of the order of 10 meters/second apparently giving pressures from about 30 kb to over 100 kb.

case, the cracks were not of concern since the material was then crushed and sieved to obtain controlled sizes of dense particles for subsequent vibratory compaction in metal tubes, giving a final net density of 85-88% for the UO_2 for use as fuel rods. While such processes were successfully developed, ceramics for reactor fuel rods are instead consolidated by conventional means.

Interest in, and investigation of, Dynapak consolidation of ceramics appears to have died out. Though possibly reduced for a while, there clearly is current interest in explosive compaction and other processing of ceramics. Of course, the most significant application of this is the conversion of BN and especially C from their hexagonal to their cubic structures for abrasives. Again, as noted earlier, these developments will not be reviewed here because of their extensive treatment in this volume and elsewhere. However, there's also been a renewed interest in explosive compaction of several ceramic materials in the last few years, as well as some use of compaction by impacting canned powders using light gas guns (primarily as a more easily controlled laboratory tool to understand explosive compaction).

Cracking is a basic problem in explosive compaction of ceramic powders, as in "Dyna-packing." Various techniques are being explored to prevent or minimize reflected shock waves which are the cause of subsequent and resultant cracking, including compaction at higher temperatures. Although Al_2O_3 powder has been reported to still crack after being shock compacted at $675^\circ C$, a SiAlON powder has been compacted to near theoretical density and crack free in a Mo tube at about $1150^\circ C$ (26), Fig. 2. In this particular case, the Mo tube was to be an integral part of the final component, but the SiAlON did not bond the Mo tube. However, post compaction bonding was readily accomplished by HIPing the component after explosive compaction (26).

Other materials that are currently being investigated by explosive compaction include metallic glasses, B, Si_3N_4 , and AlN. The latter has been explosively compacted at room temperature to greater than 92% of theoretical density (27). Although most explosive compaction experiments are on relatively small samples, there are verbal reports of Russian claims of having explosively compacted AlN to high densities and good quality in sizes up to 1 meter in diameter and 1 meter in length. Although these sizes are unconfirmed and may be exaggerated, there does seem to be general consensus that one of the potential advantages of explosive compaction are the substantial sizes that might be made, with the meter length being accepted as a more probable achievement. Diameters might be more limited, e.g. to 15-30 cm, especially where heating is required. Both the explosive compaction of titanium billets weighing as much as 12 kg and industrial explosive processing using up to almost 5000 kg of explosives per shot in industrial making of diamonds suggest that sizable bodies can be made (26).

While much of the work on explosive treatment of ceramic powder has been for direct consolidation itself as discussed

*SiAlON is an acronym which is in current use to describe oxynitrides of silicon and aluminum and related materials.

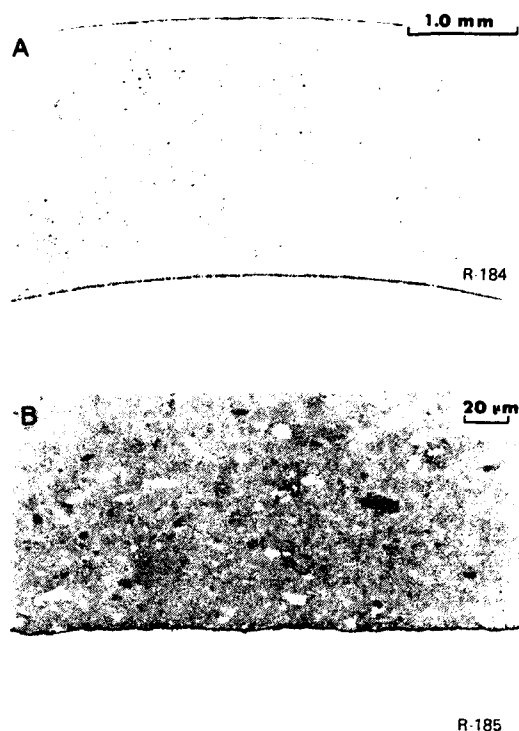


Fig. 2 - Explosively compacted SiAlON in Mo tube. A) and B) are respectively low and high magnifications showing the crack free SiAlON (dark material) and the good bonding to the inner and outer Mo tubes (light material). The Mo-SiAlON bonding was achieved by HIPing after explosive compaction. Photos courtesy of V. Linse of Battelle, Columbus.

above, the effect of explosive shock waves on subsequent processing of ceramic powders has also been investigated. Fragmentation and other effects leading to some improvement in densities in conventional cold pressing of previously shocked powder (28). It has also been reported that explosive shocking can improve the sinterability of powders (28,29). Here much of the effect is often attributed to the significant number of dislocations and other defects introduced into the structure of the material during explosive shocking leading to enhanced diffusion and material transport during subsequent sintering.

While much remains to be learned about explosive compaction, sufficient work has been done to outline basic requirements in terms of starting powder compacts. Thus, in general, intermediate green densities and intermediate particle sizes are desired. Starting densities of about 60%, often preferably obtained by isopressing, are desired. Lower densities lead to a variety of problems such as too much container wall movement, more cracking, greater shock dissipation, etc. Higher densities limit bonding achieved in a powder

compact. Much of this bonding is believed to be due to frictional heating, but other mechanisms such as explosive welding can also contribute. Clearly, frictional effects would be reduced in too dense a starting compact. Particle sizes of the order of 200 mesh are often desired. Finer particle sizes generally give too much surface area and lower starting densities. The former would again be consistent with frictional effects being important since friction would now be spread over too large an area to give adequate heating. Particles much larger than this size typically result in large pores which are more difficult to eliminate. Less is known about particle shape, except that spherical particles are generally undesirable.

HIGH PRESSURE DEFORMATION AND EXTRUSION OF CERAMICS - High pressures are required for deformation of refractory ceramics over all but the highest temperature range of behavior. Thus, for example, while highly localized, pressures under a hardness indenter reach quite high values, e.g. over 100 kb. Although crushing and cracking can be factors in the formation of hardness indents in ceramics at room or lower temperatures, most commonly the primary factor is localized plastic flow. In fact, hardness generally appears to be a reasonable estimate of the yield stress of ceramics as for metals (30).

Similarly, the measurement of the compressive strengths of dense strong ceramics at all but the highest temperatures require quite substantial pressures, e.g. 30 kb. While much of their failure under compressive loading is due to brittle fracture, ceramics appear, in fact, to have their compressive strengths limited by local plastic flow (30). Further, the superposition of hydrostatic pressure and uniaxial compressive loading can reduce or eliminate the gross fracture and other non-plastic processes such that the bulk yield stresses of ceramic materials can be achieved, as shown, for example, by the pioneering work of Bridgman (31) and a substantial number of recent studies, e.g. refs. 32-37. These, as will be discussed later, suggest possibilities for plastic working of ceramic materials.

Another area where high pressures have been used for deformation of ceramics is in their hot extrusion, (Table 1). While most of this has been by more conventional techniques which will be discussed immediately below, feasibility of extrusion by hydrostatic techniques has been demonstrated and will be discussed second. Conventional hot extrusion of ceramics has been discussed extensively elsewhere (8,9,38) and hence will be only briefly reviewed here. Ceramic extrusion has typically been done with industrial presses used for conventional extrusion of metals. The metal tooling of such presses, usually used at area reduction ratios of about 9 to 1, cannot take high temperatures. Thus, rapid loading of the heated billet in the press and rapid extrusion are necessary to minimize heat transfer into the metal tooling of the press and out of the billet, i.e. extrusion ram travel rates of the order of 5-25 cm/sec. The typical procedure has been to can the ceramic billets in a thick wall metal can, e.g. having about twice the diameter of the ceramic billets. Although the can is typically an expendable item, it may in some cases be an integral part of the end compo-

nent, as in some complex geometries of glass-steel bodies that have been extruded (8,9).

Most extrusion has been of crystalline material, especially in polycrystalline form. Although not as easy, and hence not as highly developed as extrusion of glasses, some extrusion of other than simple circular cylinders of refractory ceramics has been achieved (8,9). In general, success has been restricted to cubic materials that exhibit considerable plastic deformation well below their melting temperatures, e.g. materials such as CaO, MgO, NbC, and TiC. At least some of these cubic materials, e.g. MgO, show distinct textures, i.e. preferred orientations as a result of extrusion. Such textures can be quite important for specialized applications. Pure, noncubic materials such as Al_2O_3 and cubic materials such as $MgAl_2O_4$ which show much more limited plasticity at high temperatures have not been successfully extruded even at temperatures quite close to their melting point. While these materials might be extrudable at much lower rates, were tooling to allow this, it has not been practical. The high temperatures, usually at least 60%, and more commonly 80% of the absolute melting temperature, required for the cubic materials successfully extruded has typically resulted in their structures being mostly if not totally recrystallized on extrusion and fairly large grain sizes, e.g. $\geq 50 \mu m$. While it has been demonstrated that powders can be consolidated during the extrusion process, this complicates the extrusion, and reduces the volume per extrusion. It also can compromise the quality of the resultant extrusion, due for example, to some residual porosity and limited grain boundary bonding due to outgassing limitations.

Extrusion of metals using hydrostatic pressure from a fluid has long been recognized as advantageous for obtaining greater ductility, lower extrusion temperatures, etc. Similarly, extrusion from one hydrostatic medium into a second hydrostatic medium at lower pressure, i.e. fluid to fluid extrusion, can inhibit cracking and other degradation of extruded materials, making such fluid to fluid extrusion potentially applicable to the most intractable materials. Application of hydrostatic extrusion or fluid to fluid extrusion of ceramics would of course require fluids and temperatures well beyond those of the hydraulic fluid used in hydrostatic extrusion of metals. However, such extrusion should allow a wider range of ceramics to be extruded, or to be done at lower temperatures, making it more practical and give important results such as much finer grain size.

Two techniques were investigated by the author and colleagues (8,9,38) for high temperature hydrostatic extrusion or fluid to fluid extrusion of ceramics. Both involved salts as fluids and both generally utilized metal containers. In the first approach, solid billets were placed in cans with a salt that would be heated above its melting temperature and extruded while the salt was molten.* Various problems arising from maintaining adequate seals and properly

*This approach was spearheaded by Gerald Freidman, then of Nuclear Metals Corp. of Concord, Mass. working with the author on a NASA contract.

allowing for the expansion and outgassing of the salt on melting were not fully resolved. However, use of steel billets at lower temperatures showed that such a system could be utilized for extrusion (Fig. 3). This was followed by a successful extrusion of Mo using molten NaCl at 1100°C.



Fig. 3 - Partial extrusion of steel billet with a molten salt (heat treating salt melting at $\sim 500^\circ\text{C}$). This figure clearly shows that the billet and the can are co-extruding, but excluding the molten salt from the extruded product as desired. Note also the large asymmetrical shrinkage void from solidification of salt illustrating problems that can occur in obtaining adequate can-fill if the salt starts solidifying before the extrusion is completed.

The second approach to hydrostatic extrusion of ceramics was to use salts in their solid state, depending upon their much greater ductility than the billet being extruded to make them appear as a "quasi-fluid". A similar extrusion of steel was repeated, again using solid NaCl as the "fluid" at 700-800°C. However, the steel was also extruded into solid NaCl at $\sim 480^\circ\text{C}$. This extrusion was also successful, indicating feasibility of fluid to fluid extrusion using solid salts. Next, a Mo billet was successfully extruded using solid CaF_2 (at 1175°C) as the "fluid", but an extrusion of a Mo alloy billet failed, apparently due to too low a temperature.

To begin experiments on ceramics, marble (CaCO_3) was used. While crack-free extrusions of marble had been obtained by conventional extrusion in thick walled cans, similar extrusions with thin walled cans had resulted in cracked bodies (unpublished work of James Hunt, see Fig. 4A). Extrusion of marble in a thin wall steel can using solid NaCl as a "quasi fluid" was successful, giving an uncracked billet (Fig. 4B) further demonstrating the potential of using solid salts for hydrostatic extrusion. Next, two preliminary attempts of extruding CaO billets using CaF_2 as a "quasi fluid" (at temperatures of approximately $1200 \pm 50^\circ\text{C}$) were made. Considerable intrusion of the CaF_2 into cracks,

some of which may have been along separated grain boundaries in the CaO occurred suggesting the possible use of a thin wall metal sheet around the ceramic. Although CaO extrusions were not fully successful they further indicated potential success of this solid "quasi-fluid" approach (pioneered on the same NASA program noted earlier by James Hunt who was also a key person in developing much of the conventional ceramic extrusion discussed above).

Although the above work was not carried further because program funds were exhausted, it did show considerable possibility of successful high temperature hydrostatic extrusion of ceramics, as well as the possibility of fluid to fluid extrusion. Using actual molten salts contained in a metal can showed promise, but presented a number of difficulties associated with maintaining adequate fill of the can and adequate sealing due to large volume changes on melting and solidification, outgassing, etc. The solid "quasi fluid," approach also appeared to be quite promising and, in fact, may be potentially the better of the two. Use of solid salts may limit extrusion temperatures, since it may not be practical to accommodate first heating of the salt above its melting point and then letting it solidify in order to extrude close to the salts melting point. However, Jim Hunt's suggestion to use glasses as the fluid would appear to be particularly promising, especially based on some of his other experiments with the extrusion of glasses. Thus, while substantial work remains to be done, it does appear that it would be feasible to carry out hydrostatic extrusion of ceramics and that this may well be feasible at several hundred degrees centigrade less than the temperatures required for conventional extrusion, e.g. extrusion temperatures as low as the order of 1500°C may be possible for CaO instead of temperatures of approximately 2000°C .

FUTURE DEVELOPMENT OF HIGH PRESSURE APPLICATION TO CERAMICS

Predicting where development could or should go in a technological area that is only partially understood and explored is at best an uncertain process. However, it is worthwhile to consider some of the possibilities for future application of high pressure to ceramics, besides growth of diamond and cubic BN production. To do this, let us first consider non-explosive application of high pressures to ceramics. Although it is possible that significant development of techniques or new needs will arise which could significantly change the present limitations of non-explosive methods of dynamic compaction such as the Dynapak, these are not expected to receive significant emphasis. A basic reason for this is that explosive compaction should be able to do most, if not all, of the tasks that mechanical machines could, and possibly more, as well as do these probably at significantly less cost and in larger and more versatile sizes and shapes. Thus, the use of mechanical methods of dynamic compaction is expected to be more as a development tool, e.g. such as the present use of light gas guns.

In order to better address the issue of possible future development of explosive

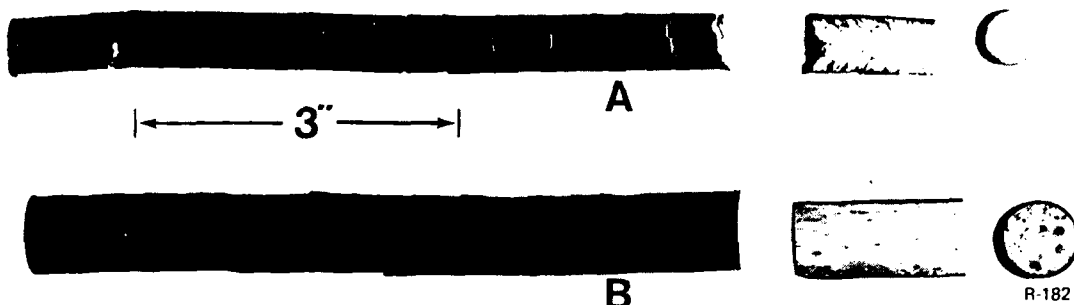


Fig. 4 - Comparison of conventional and hydrostatic extrusions of marble. As noted in the text, crack free extrusions of marble can be obtained using thick walled metal cans. However, as shown in A), if marble is extruded by conventional techniques in a thin walled metal can, substantial cracking occurs as seen on the outside surface of the extrusion, as well as in the longitudinal cross-section (middle), but not in the transverse cross-section (far right). B) shows a similar, but crack free extrusion done under hydrostatic conditions using solid NaCl at 730°C as a "fluid."

compaction of ceramic powders, it is useful to break the applications down into three broad categories. The first is treatment of powders to enhance their subsequent processing; i.e. particle size reduction to increase compaction densities and generation of defects to enhance sinterability, as noted earlier. However, it is this author's judgement that unless significant new developments are forthcoming that these applications are likely to be fairly limited. Much finer particle sizes and in general much greater control of them can be achieved by chemical means rather than by comminution with explosives. It is not clear how well defects enhance sinterability over a broad range of materials and conditions, e.g. there is a very fundamental question of whether or not much or all of the defect population introduced by explosive shock is annealed out of the powder particles long before sintering is completed. This would limit effects on later stages of sintering, which are generally critical to achieving high densities required for many technological applications. Also, one must again look at alternate routes, especially use of fine chemically produced powders which, in general, can give greater improvements in sinterability.

Consider next the second possible area of explosive shocking of powders; dynamic compaction. Specialized applications requiring dense agglomerates that can be produced without eliminating cracking may occur similar to that described for the UO₂ fuel elements made by the mechanical dynamic compaction method described earlier. There may also be some materials or developments which would allow cracks left from dynamic compaction to be healed, for example, by HIPing. However, much broader application of explosive compaction of powders is seen if techniques for generally eliminating cracking due to reverberation stresses can be found. Certainly, further work to explore the use of higher temperatures to minimize such cracking appears highly desirable as one important method to address the cracking problem.

Besides size, one of the driving forces for development of explosive compaction is its capabilities of consolidating materials at lower temperatures. This can be particularly important in making a composite component, e.g. the SiAlON-Mo component described earlier (Fig. 2).

There may be important possibilities in consolidation of bodies whose composite structure is on the microstructural scale in contrast to the macro SiAlON-Mo composite. Thus, for example, there have been spectacular improvements in toughness reported as a result of incorporating high volume fractions of fine (10 μ m dia) SiC fibers in glass matrices (39-41). Work is also underway in the author's laboratory to attempt to use these same or other similar size fibers in more refractory crystalline matrices. While progress is being made in this area, this is clearly more challenging since many of the more refractory matrices require higher processing temperatures which may often be incompatible with the temperature-mechanical limitations of the fibers. Thus, if explosive compaction will allow consolidation to, or close to, zero porosity of such composites without serious damage to the fibers, this could have significant impact on the use of explosive compaction. Further, there may be an important synergistic interaction between explosive compaction and ceramic composites. Greatly increased fracture toughness of the composite body could significantly reduce, and possibly eliminate, cracking from reverberation stresses. Thus, explosive compaction may provide enhanced opportunities for consolidation at temperatures that allow a useful composite to be made, while at the same time, the high toughness of the resultant composite inhibits cracking, allowing practical utility of explosive compaction.

The third area of explosive compaction, that of phase transformation, has of course been most widely applied, since this is the motivation in the production of diamond and cubic BN material from their softer hexagonal phases. Other important applications for such

phase transformation effects may arise. One that is of current and potentially very significant interest in the field of ceramics deals with a new mechanism of toughening, called phase transformation toughening. This has been observed to occur when metastable tetragonal ZrO_2 particles are trapped in a matrix which can be either cubic (stabilized) ZrO_2 or some other chemically compatible matrix such as Al_2O_3 . Since the transformation to the monoclinic phase (the stable phase below $\sim 1100^\circ C$) requires a volume expansion, this is inhibited by the matrix except in the vicinity of a crack under high stress (41,42). Significant energy absorption due to transformation of particles in the vicinity of high crack tip stresses provides a very important mechanism of toughening ceramics (Fig. 5). Similar

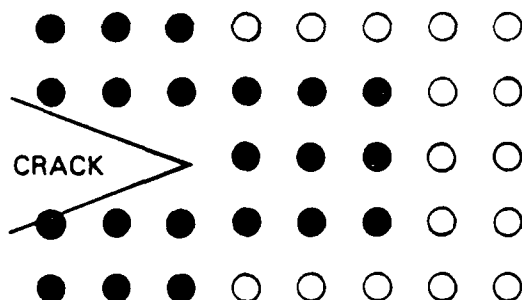


Fig. 5 - Schematic illustration of phase transformation toughening in ceramics. The concept is that a dispersed array of particles having an unstable crystal structure are inhibited from transforming to their stable crystal structure by the matrix except in the vicinity of the crack tip. There the high dilatational stresses sufficiently relaxes the matrix constraint so the particles transform to their stable crystal structure. However, as the crack propagates, transformed particles do not retransform back to their unstable structure; hence, retaining substantial stored elastic energy in themselves and the matrix due to the significant mismatch in strains between them and the matrix. This removes substantial amounts of elastic energy that would otherwise be available for crack propagation, hence, providing substantial toughening.

effects are expected from close chemical relative of ZrO_2 , namely HfO_2 . However, its transformation temperature is $1700^\circ C$ compared to $1100^\circ C$ for ZrO_2 . Thus, while there may be some application of explosive compaction to form bodies with entrapped metastable ZrO_2 particulates, it may be even more applicable to development of such bodies with entrapped metastable tetragonal HfO_2 particulates (42). In this case, high pressures would be utilized to bring about the conversion of the HfO_2 particulates originally mixed with particulates of the phase to form the matrix as the body is explosively compacted. Such transformation by pressure would thus allow processing at temperatures below the high

transformation temperature of $1700^\circ C$, possibly making such composites more practical or superior in their performance.

More generally, explosive conversion and compaction may provide a means of significantly expanding the compositions for which transformation toughening is operative. While ZrO_2 and HfO_2 are very useful, they are fairly unusual in having denser crystal structures for their high temperature phases. Thus, as discussed elsewhere (40), use of high pressure, especially explosive conversion and consolidation may be an important means of expanding the range of transformation-toughened composites. Since high pressure typically drives a phase transformation to denser crystal structures, such pressure induced transformation of particles of a phase (A) dispersed in particles of another phase (B) forming the matrix should result in the desired composite structure. Thus, conversion of A to its denser phase A', would leave A' as metastable phase particles trapped in the matrix (B).

Again, it should be noted that there is an important possibility of a synergism here between composite fabrication and explosive compaction. Thus, the compaction either makes feasible or improves the processibility of the composite while the composite makes the use of explosive compaction more practicable by inhibiting cracking due to reverberation stresses as a result of a higher toughness upon consolidation. This mechanism of toughening also shows the need and utility of phase studies to identify other ceramics amenable to transformation toughening, and in turn, use of high pressures to process them. Finally, it should be noted that the emphasis has been on phase transformation for mechanical purposes. There may be important opportunities for use of phase transformation for non-mechanical, e.g. electrical, optical, magnetic, etc. purposes which may bear investigation and development.

While high pressure deformation of ceramics is apparently not currently being explored as a means of processing them, it still does appear to have some potential use. The continued and growing interest and exploration of plastic deformation of ceramics at conventional pressures attest to this. There are two types of basic goals that have generally been sought. The first and probably more extensive is that of obtaining preferred crystallographic orientation to enhance mechanical, magnetic, electrical, or optical performance. The second area of application of conventional deformation of processing of ceramics has been to recrystallize single crystals first to introduce grain boundaries for enhanced mechanical properties, isotropy, and to obtain more versatile or practical shapes than can be grown by single crystal techniques while at the same time maintaining single crystal quality in terms of purity and the absence of porosity. Areas in which high pressure deformation of ceramics might find some applicability are to greatly increase the rate of deformation, or to significantly lower the temperature of deformation, especially in those cases where higher temperatures may bring about other undesirable changes in the material, and to give greater shapability, e.g. more complex shapes.

An example of possible uses of deforma-

tion of single crystals is the possibility of plastic deformation of partially stabilized ZrO_2 crystals that have been recently developed (40,41,43). These single crystals, grown by the practical method of skull melting, have impressive strengths; in excess of 200,000 psi (1.4 GPa) at room temperature and maintain strengths of $\sim 100,000$ psi (700 MPa) at temperatures to at least 1500°C. Conventional press forging has been shown feasible to provide some shaping of these to considerably increase the versatility of the crystal shapes that can be obtained. However, the high temperatures required at conventional pressures necessitate the use of graphite tooling which, combined with high temperatures, significantly reduces the ZrO_2 . Stresses resulting from the reduction and reoxidation present a definite problem. If this problem cannot be adequately overcome by conventional processes, then the possibility of high pressure deformation of these crystals at lower temperatures with less reduction could be an important possibility to consider.

SUMMARY AND CONCLUSIONS

Application of pressures to ceramics including high pressures has been briefly reviewed and future possible applications considered. While the use of high pressures are very important in studying the behavior of ceramics, e.g. their phase relationships and their deformation behavior, emphasis was placed on their use in processing since this is likely to be the most important area for future growth. The emphasis was thus on powder consolidation and secondarily, on the possibilities of plastic deformation as a processing techniques. Both static and dynamic consolidation of powders were briefly reviewed showing that significant problems of outgassing can occur. Dynamic powder compaction, primarily by explosive techniques, was judged most promising. Explosive consolidation of composite bodies, such as fiber composites or use of shock transformation of a purposely incorporated second phase for transformation toughening, was cited as a possible important area due in part to a suggested synergism between the composites and explosive consolidation.

Application of more conventional type hot extrusion to ceramic materials was reviewed showing it was feasible with thick wall metal cans at quite high pressures and temperatures. Further, experiments suggesting the possibility of hydrostatic, and possibly even fluid-to-fluid, extrusion of ceramics at temperatures much higher than those achievable with conventional hydraulic fluids were reviewed. While use of molten salts showed some promise, use of solid salts or glasses as fluids was felt to be more promising. If such techniques can be further developed to achieve extensive plastic flow at temperatures significantly below that required for the conventional deformation, e.g. extrusion of CaO and MgO at temperatures of 2000 and 2200°C, they could find important application. Application of hydrostatic deformation to partially stabilized ZrO_2 crystals was suggested as a possible important application.

Clearly the future direction of high pressure application to processing of ceramics will continue to depend on the ingenuity

to recognize the special combination of circumstances of expected or known material behavior and its potential for meeting particular needs, often times of a high specialized nature.

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REFERENCES

1. F. H. Norton, "Elements of Ceramics," Second Edition, Addison Wesley Publishing Co. (1974).
2. J. T. Jones and M. F. Berard, "Ceramics: Industrial Processing and Testing," Iowa State Un. Press, Ames, Iowa (1972).
3. Committee on Ceramic Processing, "Ceramic Processing," National Academy of Sciences, Wash., D.C. (1968).
4. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, "Introduction to Ceramics," Second Edition, John Wiley & Sons Pub. Co. (1960).
5. R. M. Fulrath, "Hot Forming Process," Ceramic Bull. Vol. 43, #12, 880-885 (1964).
6. S. D. Brown, O. E. Accountius, H. W. Carenter, T. F. Schroeder, and M. J. Seric, "Critical Evaluation of Ceramic Processing at Subconventional Temperatures," Final Report (16 June 1966-15 June 1967) to Air Force Mat. Lab. under Contract No. AF33(615)-5124.
7. B. R. Emrich and S. D. Brown, "10 New Ways to Fabricate Ceramic Parts," Materials Engineering, 72-78 (1968).
8. R. W. Rice, "Hot Forming of Ceramics," pp 203-250 in Ultrafine-Grain Ceramics, Syracuse Un. Press (1970).
9. R. W. Rice, "Hot-Working of Oxides," High Temperature Oxides, Vol 3, pp. 235-280, Academic Press (1970).
10. R. W. Rice, "Deformation, Recrystallization, Strength and Fracture of Press-Forged Ceramic Crystals," J. Am. Ceram. Soc., Vol. 55, #2, 90-97 (1972).
11. E. A. McGuire, Jr. and R. L. Gentilman, "Press Forging Small Domes of Spinel," Ceramic Bull., Vol. 60, #2, 255-256 (1981).
12. P. W. Montgomery, H. Stromberg, and G. Jura, "Sintering of Refractory Materials at Room Temperature by High Pressures," in Solid Surfaces and the Gas-Solid Interface-Advances in Chemistry No. 33, Am. Chem. Soc., p. 18-22 (1961).

13. T. Vasilos and R. M. Spriggs, "Microstructure in Oxides," in *Sintering and related Phenomena*, G. C. Kuczynski, N. A. Hooton, and C. G. Gibben, eds., Gordon and Breach, 301-27 (1967).
14. R. W. Rice, "The Effect of Gaseous Impurities on the Hot Pressing and Behaviour of MgO, CaO and Al₂O₃," *Proc. British Ceram. Soc.*, 99-123 (1969).
15. J. S. Madeau, "Very High Pressure Hot Pressing of Silicon Carbide," *Ceramic Bull.*, Vol. 52, #2, 170-174 (1973).
16. S. Prochazka and W. A. Rocco, "High-Pressure Hot-Pressing of Silicon Nitride Powders," pp. 615-625 in *Processing of Crystalline Ceramics*, Vol. 11, eds. Palmour, Davis and Hare, Plenum Press, NY (1978).
17. M. Shibata, N. Kinomura, and M. Koizumi, "High-Pressure Sintering of Silicon Nitride," *Ceramurgia International*, Vol. 6, n.4, 146-47 (1980).
18. R. L. Hallae, "High Energy Forming of Glasses and Ceramics," *Ceramic Bull.*, Vol. 42, #11, 711 (1963).
19. D. J. Bowers, "Miscellaneous Forming Methods," *Ceramic Bull.*, Vol. 44, #2, 145-150 (1965).
20. D. W. Brite and C. A. Burgess, "High Energy Rate Pneumatically Impacted UO₂-PuO₂ Fuels," *Trans. Am. Nuc. Soc.*, 7, 408 (1964).
21. S. Goldsmith, et al, "A Physically Mixed and Impacted UO₂-PuO₂ Fast Reactor Fuel," *Trans. Am. Nuc. Soc.*, 7, 409 (1964).
22. R. E. Sharp, et al, "UO₂-PuO₂ Fuel Elements for the Plutonium Recycle Demonstration Experiment," *Trans. Am. Nuc. Soc.*, 7, 403 (1964).
23. D. W. Brite and K. R. Sump, "Fabrication of Shapes by Pneumatic Impaction," U. S. Patent #3,213,163, Oct. 19, 1965.
24. D. W. Brite and K. R. Sump, "Cermat Materials and Process of Making," U. S. Patent #3,276,867, Oct. 4, 1966.
25. J. R. Hegue and D. W. Brite, "Fabrication of Materials by High Energy-Rate Impaction," U. S. Patent #3,344,209, Sept. 27, 1967.
26. V. D. Linse, Battelle Columbus Lab, cent #3,344,209, Sept. 27, 1967.
26. V. D. Linse, Battelle Columbus Lab, Private Communication, 1981.
27. C. F. Cline, Lawrence Livermore Lab, Private Communication, 1981.
28. O. R. Bergmann and J. Barrington, "Effect of Explosive Shock Waves on Ceramic Powders," *J. Am. Ceram. Soc.*, Vol. 49, #9, 502-507 (1966).
29. K. Kawada and A. Onodera, "Effect of Residual Strain on High Pressure Densification of Monoxide Ceramics," *Ceramic Bull.*, Vol. 59, #11, 1151-52 (1980).
30. R. W. Rice, "The Compressive Strength of Ceramics," *Materials Science Research*, Vol. 5, ed. W. Wurth Kriegel, Plenum Press, NY, 195-229.
31. P. W. Bridgman, "Studies in Large Plastic Flow and Fracture," p. 120, McGraw Hill, New York (1952).
32. C. W. Weaver and M. S. Paterson, "Deformation of Cube-Oriented MgO Crystals Under Pressure," *J. Am. Ceram. Soc.*, Vol. 52, #6, 293-302 (1969).
33. M. S. Paterson and C. W. Weaver, "Deformation of Polycrystalline MgO Under Pressure," *J. Am. Ceram. Soc.*, Vol. 53, #8, 463-471 (1970).
34. T. A. Auten and S. V. Radcliffe, "Deformation of Polycrystalline MgO at High Hydrostatic Pressure," *J. Am. Ceram. Soc.*, Vol. 59, #5, 249-253 (1976).
35. T. A. Auten and S. V. Radcliffe, "Flow Stress of MgO Single Crystals Compressed Along [100] at High Hydrostatic Pressures," *J. Am. Ceram. Soc.*, Vol. 59, #1-2, 40-43, Jan-Feb 1976.
36. J. Crampon and B. Escaig, "Mechanical Properties of Fine-Grained Magnesium Oxide at Large Compressive Strains," *J. Am. Ceram. Soc.*, Vol. 63, No. 11-12, 680-686, Nov-Dec 1980.
37. J. Castaing, J. Cadot and S. Kirby, "Prismatic Slip of Al₂O₃ Single Crystals Below 1000°C in Compression Under Hydrostatic Pressure," submitted to *J. Am. Ceram. Soc.* Oct. 1980.
38. R. W. Rice, J. G. Hunt, G. I. Friedman, and J. L. Sliney, "Identifying Optimum Parameters of Hot Extrusions," Final Report under NASA Contract NAS7-276 (1968).
39. K. M. Prewo and J. J. Brennan, "High-Strength Silicon Carbide Fiber Reinforced Glass-Matrix Composites," *J. Mat. Sci.* 15, pp. 463-68 (1980).
40. R. W. Rice, "Ceramic Composites-Processing Challenges," in press, *Ceramic Engineering and Science Proceedings* (1981).
41. R. W. Rice, "Mechanisms of Toughening in Ceramic Matrix Composites."
42. A. C. Evans and A. H. Heuer, "Review: Transformation Toughening in Ceramics and Martensitic transformation in Crack-Tip Stress Fields," *J. Am. Ceram. Soc.* 63 (5-6) 241-248 (1980).
43. R. P. Ingel and R. W. Rice, "Room Temperature Strength and Fracture of ZrO₂-Y₂O₃ Single Crystals," submitted to *Ceramic Communications*.

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